

Layered Calcium Phenylphosphonate as a Filler for Polymer Nanocomposites

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Theoretical Background

Layered organophosphonates

Hybrid organic-inorganic materials with a layered structure. It means that there are strong covalent bonds within the layers but the layers hold together only through van der Waals interactions.

This arrangement makes them ideal candidates for:

- Intercalation (= accommodating suitable molecules in the space between the layers)
- Exfoliation (= peeling the layers apart)

Versatility of the organic part is beneficial for tuning properties of these materials and presence of organic groups improves compatibility with polymer matrix and enables to use these materials as fillers for composites.

Exfoliation

Exfoliation in general is a process of disintegration of a layered material when thin sheets of a material are completely separated from the bulk. To separate the layers it is necessary to overcome the cohesive forces between the adjacent layers. In principle there are two options^[1]: It is possible to “tear” the layers apart by a perpendicular force or to use a shear force, which is parallel to the layers, and slide the layer away from the others. Nowadays, the most popular method is the so called „Liquid-based exfoliation^{[2]“} where the mechanical forces are combined with chemical interactions with molecules of a solvent and a surfactant (e.g. in an ultrasound bath). In other words, exfoliation is one of the top down methods for the preparation of nanomaterials.

Experimental & Results

Synthesis of Calcium Phenylphosphonate (CaPhP)^[3]

First, phenylphosphonic acid is dissolved in water and pH of the obtained solution is adjusted to 8-9 by adding concentrated ammonia solution, then CaCl₂ as a source of metal dissolved in water in a molar ratio 1:1 according to phosphonic acid is added. After 30 minutes of stirring the white precipitate is collected by filtration and washed with water until the neutral pH. It is possible to dry the sample in air or store it wet in a form of slurry. The shape of the particles and the structure of CaPhP are in Figures 1 and 2, respectively.

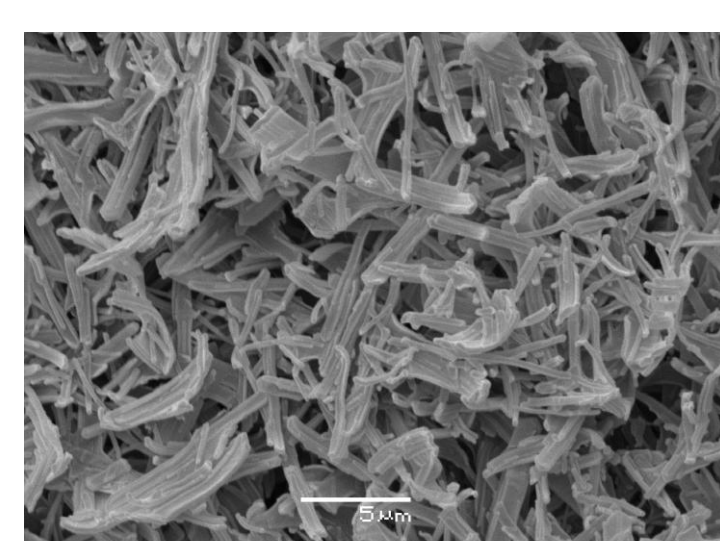


Figure 1

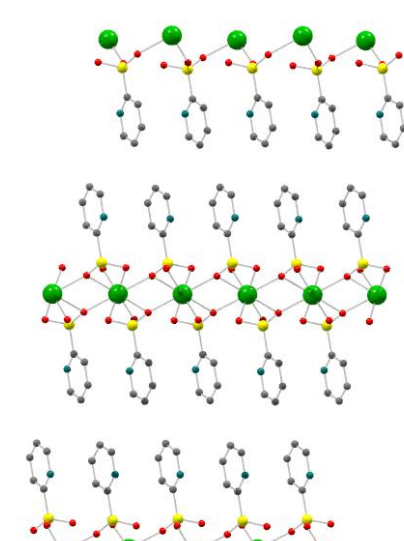


Figure 2



Figure 3

Exfoliation of CaPhP

For exfoliation of the CaPhP particles a Liquid-based exfoliation method was used. In a typical experiment (Figure 3)

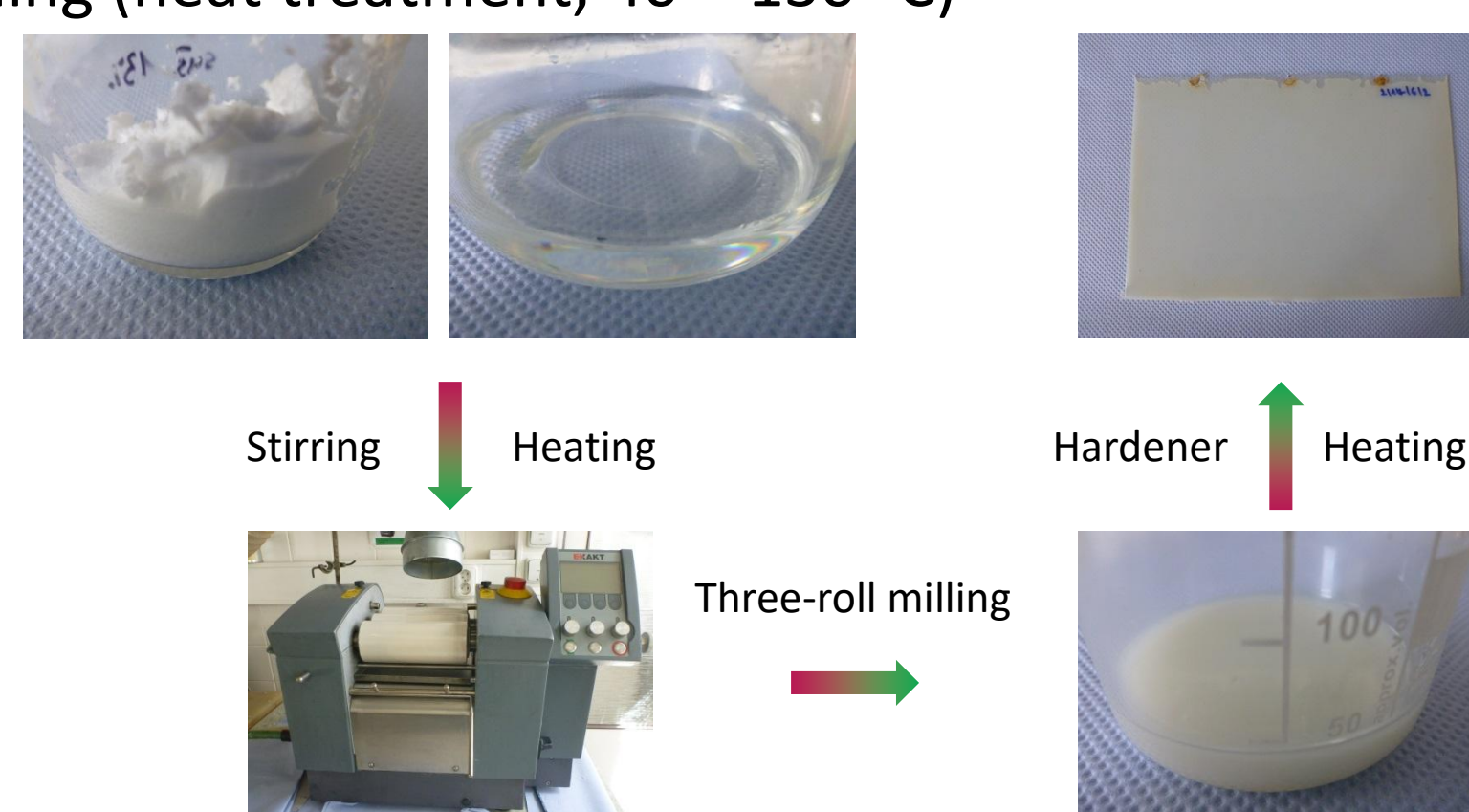
- 50 mg of CaPhP and
- 50 ml of propan-2-ol

were put in a round bottom flask and sonicated in an ultrasound bath with frequency 37 kHz for one hour. However, different sonication times were also tested.

Preparation of the composite

Calcium phenylphosphonate was tested as a filler into epox 520 which is an epoxy resin based on bisfenol-A compound. Preparation of the composite consists of several steps:

1. Dispersion of the particles in the epoxy resin (mechanical stirring)
2. Homogenization (the three-roll milling)
3. Mixing with a hardener
4. Hardening (heat treatment, 40 – 130 °C)



Visual observation (Figure 4)

- Dispersion stability
- Stable for weeks
- Tyndall effect (presence of small particles)



Figure 4

Dynamic light scattering

- Change of the particle size with sonication time
- The size distribution is bimodal in all cases (Figure 5)
- Selection of the samples for AFM measurements

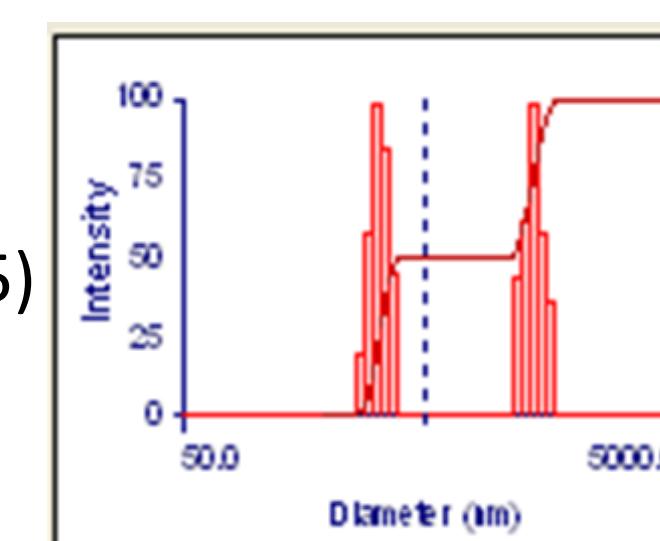


Figure 5

Atom force microscopy (Figure 6)

- Confirmation of the layered structure
- Thickness of the particles

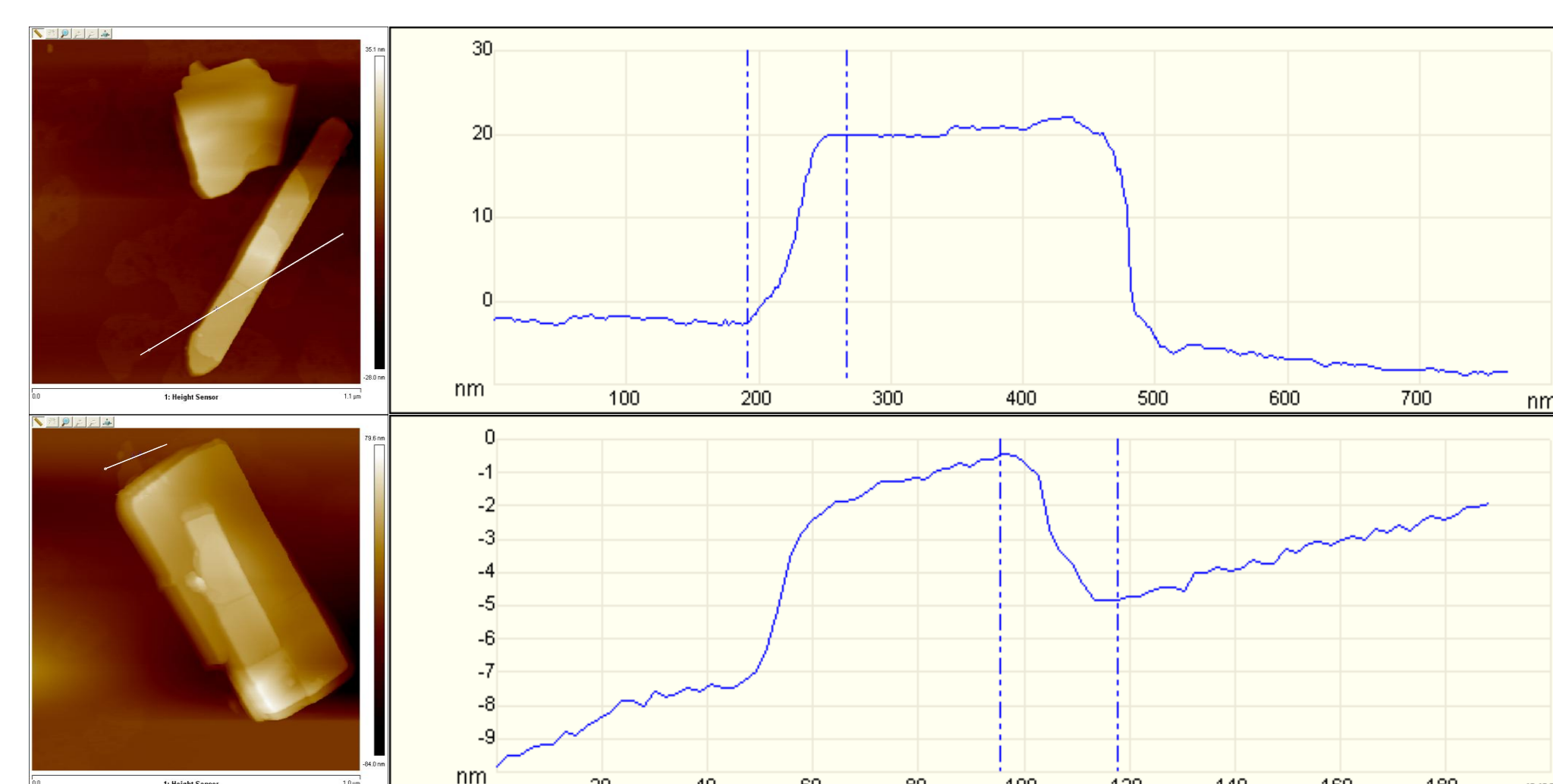


Figure 6

Optical microscopy (Figure 7)

- Particles distribution within the polymer matrix
- No agglomerates, homogenous distribution

Tensile testing

- Properties comparable to the original polymer

Flammability (Limiting oxygen index)

- 10 % improvement

Barrier properties

- In progress

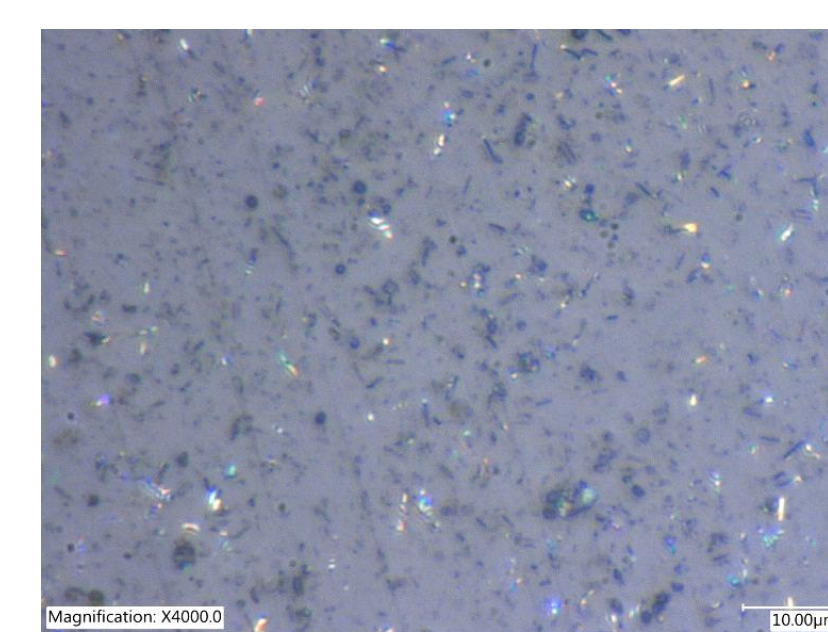


Figure 7

Conclusion

- It is possible to exfoliate particles of CaPhP via sonication in propan-2-ol
- This procedure leads not only to exfoliation but also to fragmentation of the particles
- The particles of calcium phenylphosphonate exhibit great compatibility with the polymer matrix of epox 520

Acknowledgement

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Literature

- [1] Yi, M. and Z. G. Shen (2015). „A review on mechanical exfoliation for the scalable production of graphene” Journal of Materials Chemistry A 3(22): 11700-11715.
- [2] Nicolosi, V., M. Chhowalla, et al. (2013). „Liquid Exfoliation of Layered Materials” Science 340 (6139)
- [3] Svoboda, J., V. Zima, et al. (2005). Inorganic Chemistry 44: 9968-9976